

PATENT SPECIFICATION

628,686



Convention Date (United States of America): Oct. 29, 1943.

Application Date (in United Kingdom): Aug. 19, 1947. No. 22960/47.

Complete Specification Accepted: Sept. 2, 1949.

Under Rule 17A of the Patents Rules 1939-47, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1946, became operative on Aug. 19, 1947.

Index at acceptance:—Class 2(iii), B1h.

COMPLETE SPECIFICATION

Production of Butadiene

ERRATA

SPECIFICATION No. 628,686.

Page 1, line 27, after "a" insert "cheap method for producing it from rela-"

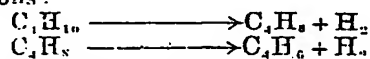
Page 2, lines 5—8, after "the" delete "butylene formed in the first stage is dehydrogenated to butadiene and a separation unit wherein the"

THE PATENT OFFICE,
13th March, 1950.

means having physical characteristics similar to natural rubber.

25 The amount of butadiene used in organic syntheses has been limited to a great extent by the non-availability of a
30 tively cheap raw materials. The most common method formerly used consisted of starting with acetylene and carrying out various chemical reactions until butylene glycol was obtained which was subsequently dehydrated to butadiene. More
35 recently butadiene has been obtained in commercial quantities in an operation which is economically feasible by the catalytic dehydrogenation of normal butane.

40 The dehydrogenation of normal butane to butadiene involves the following two reactions:



45 In view of the equations given above, it would be expected that most efficient operation for the production of butadiene from butane would be a two-stage operation in which butane was first converted to butylene and the butylene subsequently
50 converted to butadiene in a separate reaction zone. The prior art, best exemplified

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the first stage, and the butylenes separated from the reaction products of the first stage are further converted to butadiene in the second dehydrogenation operation.

The extent of the improvement obtained by the operation of this invention is clearly shown in the examples included
80 hereinafter in this specification.

Thus, the process according to the present invention comprises introducing normal butane into a first dehydrogenation zone and therein catalytically dehydrogenating only a portion of said
85 normal butane to normal butylene and butadiene, the yield of butadiene being from about 10 to about 30 volume per cent. of the normal butane charged, separating
90 the normal butylene from the resultant products, introducing the thus separated normal butylene into a second dehydrogenation zone and therein catalytically dehydrogenating normal butylene to
95 butadiene, and recovering butadiene formed in the first and second dehydrogenation zones.

In effect, the present invention utilizes three units which are cooperatively interrelated to one another. These units are a
100 first stage dehydrogenation unit which

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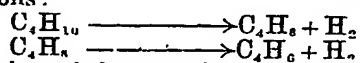
We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 310, South Michigan Avenue, Chicago, Illinois, United States of America, (Assignees of CHARLES CHURCHILL WATSON, a citizen of the United States of America, of 2408, Kendal Street, Madison 5, Wisconsin, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of butadiene and is more specifically concerned with the catalytic dehydrogenation of normal butane to form butadiene.

Butadiene is extensively employed as the starting material in many organic syntheses and is of considerable value in the production of high molecular weight polymers having physical characteristics similar to natural rubber.

The amount of butadiene used in organic syntheses has been limited to a great extent by the non-availability of a tively cheap raw materials. The most common method formerly used consisted of starting with acetylene and carrying out various chemical reactions until butylene glycol was obtained which was subsequently dehydrated to butadiene. More recently butadiene has been obtained in commercial quantities in an operation which is economically feasible by the catalytic dehydrogenation of normal butane.

The dehydrogenation of normal butane to butadiene involves the following two reactions:



In view of the equations given above, it would be expected that most efficient operation for the production of butadiene from butane would be a two-stage operation in which butane was first converted to butylene and the butylene subsequently converted to butadiene in a separate reaction zone. The prior art, best exemplified

by the United States patent No. 2,209,215, is primarily concerned with this type of operation.

It is an object of the present invention to provide an improved process for the production of butadiene from butane in which the yield of butadiene and the degree of efficiency of the reaction that is obtained are decidedly superior to those obtained by the processes of the prior art.

It is another object of the invention to provide a process which has increased flexibility and which can process satisfactorily any type of butane-butylene charging stock.

It has been discovered that contrary to expectations, a more efficient operation which produces more butadiene per unit of butane charged may be obtained by employing a two-stage operation in which normal butane is converted to substantial quantities of butadiene and butylene in the first stage, and the butylenes separated from the reaction products of the first stage are further converted to butadiene in the second dehydrogenation operation.

The extent of the improvement obtained by the operation of this invention is clearly shown in the examples included hereinafter in this specification.

Thus, the process according to the present invention comprises introducing normal butane into a first dehydrogenation zone and therein catalytically dehydrogenating only a portion of said normal butane to normal butylene and butadiene, the yield of butadiene being from about 10 to about 30 volume per cent. of the normal butane charged, separating the normal butylene from the resultant products, introducing the thus separated normal butylene into a second dehydrogenation zone and therein catalytically dehydrogenating normal butylene to butadiene, and recovering butadiene formed in the first and second dehydrogenation zones.

In effect, the present invention utilizes three units which are cooperatively inter-related to one another. These units are a first stage dehydrogenation unit which

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produces butadiene and butylene from normal butane, a second dehydrogenation unit wherein the butylene formed in the first stage is dehydrogenated to butadiene and a separation unit wherein the butylene formed in the first stage is dehydrogenated to butadiene and a separation unit wherein the reaction products from both the first and second dehydrogenation units are processed to separate the desired butadiene, the normal butane to be recycled to the first dehydrogenation unit, the butylene to be charged to the second dehydrogenation unit and the by-products such as isobutane and lower molecular weight hydrocarbons such as methane, ethylene, ethane, propylene and propane, which are removed from the system.

It has also been found that the cost of separating the butadiene per unit of weight is dependent primarily on the quantity of butadiene being introduced into the separation unit. Increasing the concentration of butadiene entering said unit produces a pronounced decrease in the separation cost. The operation of the present invention takes full advantage of this decrease in separation costs since both dehydrogenation steps are producing substantial quantities of butadiene.

The catalysts which may be employed in the dehydrogenation operations may comprise any of the well known dehydrogenation catalysts such as chromium oxide, molybdenum oxide or vanadium oxide supported by alumina in either the powdered, granular or shaped forms such as pellets or spheres. It is usually desirable when employing these catalysts to incorporate a small amount of magnesia or zinc oxide in the composite to improve the thermal stability of these catalysts. The same catalysts may be used in each stage or different catalysts may be employed in each stage. Catalysts comprising a composite of a major proportion of alumina and minor proportions of barium oxide and potassium oxide or a composite of a major proportion of magnesia and minor proportions of iron oxide, copper oxide and potassium oxide are particularly effective for the conversion of butylene to butadiene, especially if superheated steam is introduced along with the charge to effect a lowering of the partial pressure of the butylene in the reaction zone.

The invention is explained in more detail in connection with the description of the accompanying drawing which illustrates in a conventional diagrammatic flow chart one method of conducting the operation.

Referring to the drawing, normal butane fresh feed along with the recycled

normal butane obtained as hereinafter set forth is introduced through line 1 into dehydrogenation zone 2 wherein it is contacted with a dehydrogenation catalyst comprising alumina and chromia at a temperature within the range of about 565 to about 675° C. under an absolute pressure of 0.05 to about 0.5 atmospheres. The charge rate through the reaction zone will be dependent to a certain extent upon the temperature and pressure chosen but will ordinarily be within the range of space velocities of about 200 to about 1000 volumes of gas per volume of catalyst per hour. The actual conditions are selected from these ranges to produce a yield of butadiene of about 10 to 30 volume percent of the butane charged. The reaction products comprising unconverted normal butane, butadiene and butylene, hydrogen and a small portion of decomposition products such as methane, ethane, ethylene, propane and propylene leave dehydrogenation zone 2 through line 3 and are directed through line 3 into separation zone 4 wherein the light gases, butadiene and butylenes are separated from the unconverted normal butane. The unconverted normal butane is recycled through line 10 into line 1 as hereinbefore set forth. The butadiene, along with butadiene formed in dehydrogenation zone 6 as hereinafter set forth, is withdrawn from the separation zone through line 9, cooled and collected in any manner well known to those skilled in the art.

Separation zone 4 may comprise any of the well known means for separating C₄ hydrocarbon mixtures into the individual C₄ hydrocarbons such as, for example, precise fractional distillation, solvent extraction and azeotropic distillation with azeotrope-forming materials such as furfural. The separated butylenes are directed from separation zone 4 through lines 5 into a second dehydrogenation zone 6 wherein a substantial portion of the normal butylene is converted into butadiene.

The operating conditions employed in dehydrogenation zone 6 are dependent to a considerable extent upon the type of catalyst being used in said zone. When a composite comprising a major proportion of magnesia and minor proportions of iron oxide, copper oxide and potassium oxide or a composite of alumina with boria and potassium oxide is employed, superheated steam is introduced into the reaction zone to give a total pressure of about 0.25 to 3.5 atmospheres above atmospheric pressure while maintaining the partial pressure of the normal butylene at about 0.05 to about 0.5 atmospheres absolute. The temperature utilized in dehydrogenation zone 6 is dependent somewhat upon the catalyst but

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is ordinarily within the range of about 565 to 675° C. at a space velocity measured as volumes of gas per volume of catalyst per hour of about 200 to about 2000. The yield of butadiene per pass is maintained within the range of about 15 to 30 percent based on the butylenes charged.

During the dehydrogenation reaction in zones 2 and 6, some isomerization occurs producing iso-C₄ hydrocarbons. Since butadiene cannot be produced from the iso-C₄ hydrocarbons because of their molecular structure, it is advantageous to remove these isomers from the system to prevent their build-up in the streams being charged to the dehydrogenation catalyst. These isomeric by-products are removed from the separation zone through line 8 and are cooled and condensed and recovered as a product of the reaction. The reaction products from dehydrogenation zone 6 are directed through line 7 into separation zone 4 wherein the desired C₄ fractions are removed therefrom.

In case the original charging stock contains C₄ olefins in any substantial quantity, this charge may be introduced to line 11 and therefrom into line 3 through which it is directed into the separation zone 4, wherein the necessary separation of olefins and paraffins is effected, or alternatively, although not shown in the drawing, the charging stock may be introduced directly into the separation zone. The reaction in either dehydrogenation zone may be conducted in either the fluid, fixed or moving catalyst bed type of operation. When employing a fixed bed type of operation, the catalyst may be disposed in externally heated tubular elements connected in series or parallel. The external heating may be accomplished by indirect heat exchange by hot combustion

gas or other heat-carrying media such as for example, molten salts or superheated steam.

During the dehydrogenation reaction, considerable amounts of carbonaceous materials are laid down upon the catalyst and after the catalyst has been used for some time it is necessary to remove these carbonaceous deposits to restore the catalyst activity. These carbonaceous materials are ordinarily removed by introducing a heated stream of air or air diluted with combustion gases to burn off the carbonaceous deposit. Although the description of the drawing has been concerned with only two dehydrogenation zones it is, of course, obvious that for more truly continuous operation, it is necessary to employ at least two reactors for each dehydrogenation operation so that the catalyst in one reactor may be regenerated by oxidation while the other is being processed.

The following examples give comparative results obtained when employing a conventional two-stage operation wherein butane is partially converted to butylene in the first stage and the reaction products from the first stage are charged to the second stage to produce butadiene, and a process in accordance with the present invention wherein butane is converted to butadiene and butylene in the first stage and the butylene thus formed is subsequently converted to butadiene in the second stage. It is obvious from a study of the data given below that the process as practiced in accordance with the present invention is considerably improved over that of the prior art as to the actual yield of butadiene by weight of the butane charged.

TABLE.

		Example I Conventional Operation		Example II Improved Operation	
		1	2	1	2
90	Stage - - - - -	1	2	1	2
	Absolute pressure, mm. Hg. - - -	Atmos.	80	80	80
	Catalyst temperature, ° C. - - -	593	635	635	635
	Conversion *Mol. % per pass - - -	34	30	30	30
	Space velocity** - - - - -	250	725	250	2000
	Charge: Mol. %				
95	C ₄ H ₁₀ - - - - -	2.0	45.0	2.0	95.0
	C ₄ H ₁₀ - - - - -	98.0	55.0	98.0	5.0
	Product, C ₄ 's, Mols./100 mol. feed to stage				
	C ₄ H ₆ - - - - -	0.0	20.4	15.0	22.5
100	C ₄ H ₈ - - - - -	33.0	30.0	41.0	63.0
	C ₄ H ₁₀ - - - - -	33.0	40.0	29.0	7.0
	Overall Efficiency - - - - -		45.0		63.8
	*Defined here as mols. C ₄ H ₆ —C ₄ H ₈ decomposed per 100 mols. C ₄ H ₁₀ — C ₄ H ₁₀ feed to each stage.				
105	**Defined as volumes of feed at standard pressure and temperature conditions per volume of catalyst space per hour.				

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It is to be noted that the actual yield of butadiene in the improved operation is about 18.8% greater. The percent increase in the yield is about 41.8%.

6 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

10 1. A process for the production of butadiene which comprises introducing normal butane into a first reaction zone and therein catalytically dehydrogenating only a portion of said normal butane to
15 normal butylene and butadiene, the yield of butadiene being from about 10 to about 30 volume percent of the normal butane charged, separating the normal butylene from the resultant products, introducing
20 the thus separated normal butylene into a second reaction zone and therein catalytically dehydrogenating normal butylene to butadiene, and recovering butadiene formed in said first and second reaction
25 zones.

2. Process as claimed in claim 1 further characterized in that normal butane is dehydrogenated into normal butylene and butadiene in the first reaction zone at
30 a temperature of from about 565 to about 675° C., an absolute pressure of from about 0.05 to about 0.5 atmospheres, and a gaseous hourly space velocity of from about 200 to about 1000, and the normal
35 butylene is dehydrogenated in the second reaction zone at a temperature of from about 565 to about 675° C., an absolute pressure of from about 0.05 to about 0.5 atmospheres, and a gaseous hourly space
40 velocity of from about 200 to about 2000.

3. Process as claimed in claim 1 or 2, further characterized in that the yield of butadiene in the second reaction zone is maintained at from about 15 to about 30
45 percent of the butylene charged to said zone.

4. Process as claimed in any of the claims 1 to 3, further characterized in that
50 the reaction products obtained in the first reaction zone and comprising normal butylene, butadiene, and unconverted normal butane, are supplied to a separation zone, a butadiene fraction, a normal butane fraction and a normal butylene

fraction are separated in said separation
55 zone, said normal butylene fraction is introduced to the second reaction zone, reaction products obtained in said second reaction zone and comprising butadiene, a
60 minor amount of normal butane formed in the second dehydrogenation step, and unconverted normal butylene are introduced into said separation zone, the normal butane fraction obtained in said separation zone is recycled to the first reaction
65 zone, and said butadiene fraction is recovered.

5. Process as claimed in any of the claims 1 to 4, further characterized in that
70 a butane-butylene charging stock, the butadiene-containing dehydrogenation product from the first reaction zone, and the butadiene-containing dehydrogenation product from the second reaction zone are introduced into a separation zone, a normal
75 butane fraction, a normal butylene fraction, and a butadiene fraction are separated from said charging stock and dehydrogenation products in said separation zone, said normal butane fraction is
80 supplied to the first dehydrogenation reaction zone, said normal butylene fraction is introduced into the second dehydrogenation reaction zone, and said butadiene fraction is recovered as the principal product of the process.
85

6. Process as claimed in any of the claims 1 to 5, wherein the dehydrogenation of normal butane into normal butylene and butadiene in the first reaction
90 zone is effected in the presence of a catalyst comprising alumina and chromia and the dehydrogenation of normal butylene in the second reaction zone is effected in the presence of superheated steam and a
95 catalyst comprising a major proportion of magnesia and minor proportions of iron oxide, copper oxide and potassium oxide.

7. The process for the production of butadiene substantially as hereinbefore described with reference to the attached
100 drawing.

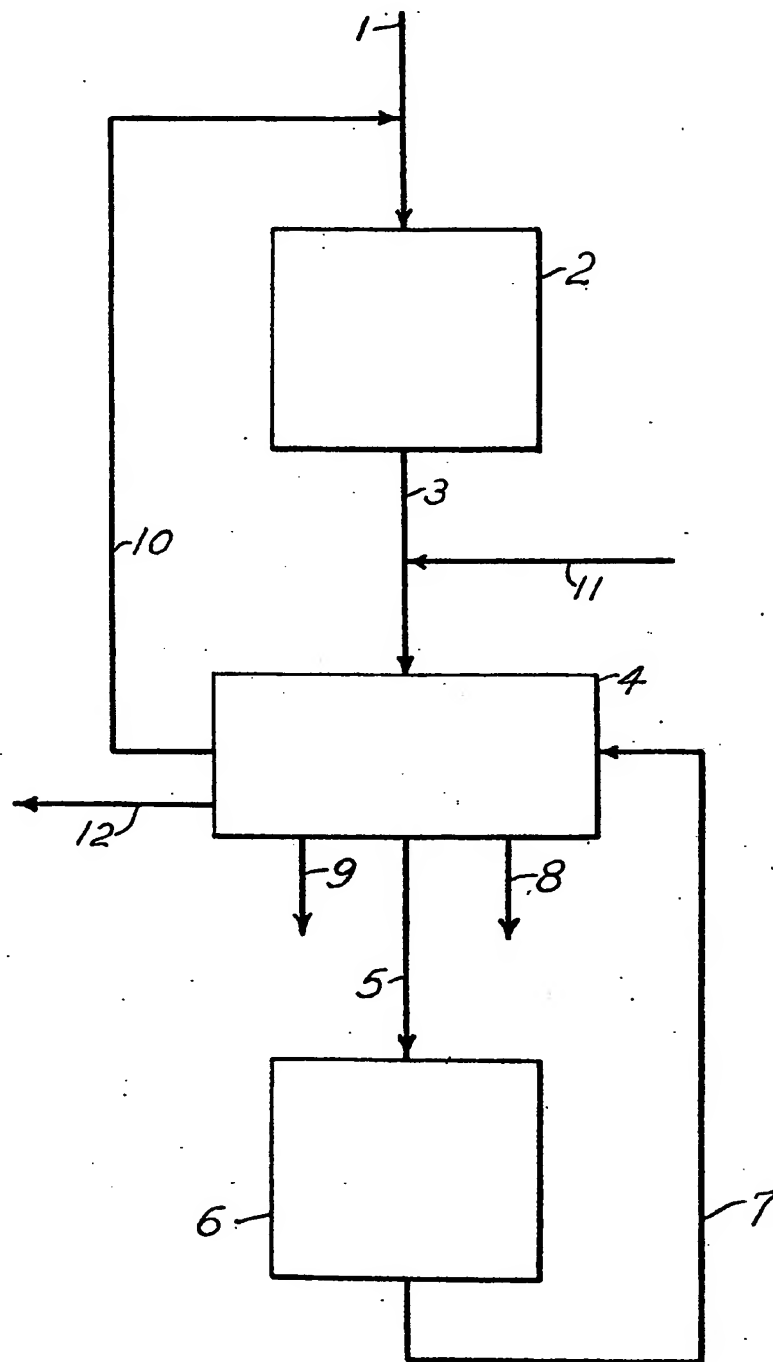
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[This Drawing is a reproduction of the Original on a reduced scale.]



H.M.S.O. (Ty.P.)

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